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TITLE: Radioactive Wastes Dispersed in Stabilized Ash Cements

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Radioactive Wastes Dispersed in Stabilized Ash Cements

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I. INTRODUCTION

One of the most widely-used methods for the solidification/stabilization (S/S) of low-level radwaste is by incorporation into Type-I/II ordinary portland cement (OPC). OPC, as an immobilization matrix, has many desirable properties, which are listed in Table 1. Also listed in the table are several disadvantages associated with cement as a wasteform. Several of these shortcomings have been successfully addressed, however, with the help of a recent innovation in OPC processing. Treating of OPC with supercritical fluid carbon dioxide ($SCCO_2$) has been shown to significantly increase the density, while simultaneously decreasing porosity. In addition, the process significantly reduces the hydrogenous content, reducing the likelihood of radiolytic decomposition reactions. This, in turn, permits increased actinide loadings with a concomitant reduction in disposable waste volume.

Table 1. Advantages and disadvantages to the use of OPC as a radwaste immobilization matrix

Advantages	Disadvantages
• good mechanical properties • adequate radiation stability • inexpensive • non-combustible • good thermal stability • easy to process and handle • tolerant to a wide range of waste types • provides some measure of shielding	• porosity/leachability • radiolytic reactions (gas generation) • increased waste volume • anticipated shortage of raw material

In this article, we will discuss the combined use of fly-ash-modified OPC and its treatment with $SCCO_2$ to further enhance immobilization properties. We begin with a brief summary of current cement immobilization technology in order to delineate the areas of concern. Next, supercritical fluids are described, as they relate to these areas of concern. In the subsequent section, we present an outline of our results on the application of $SCCO_2$ to OPC, and its effectiveness in addressing these problem areas. Lastly, in the final section, we proffer our thoughts on why we believe, based on the OPC results, that the incorporation of fly ash into OPC, followed by supercritical fluid treatment, can produce highly efficient wasteforms.

II. STATE OF THE CURRENT TECHNOLOGY

The current practice at LANL for stabilizing low-level radwaste involves casting of OPC inside 55-gallon drums. Such cemented wasteforms are intended for transfer to the Waste Isolation Pilot Plant (WIPP) for permanent underground storage. The cemented wasteforms are transported to WIPP using the TRUPAC II container, which can accommodate up to fourteen individual drums. In order to meet Department of Energy (DOE) transportation requirements,[1,2,3] however, the individual cemented wasteforms must satisfy several regulatory requirements. These requirements prevent the occurrence of potentially flammable concentrations of gases within the container as well as the generation of unacceptably large internal pressures of non-flammable gases. These controls take the form of restrictions on the packaging, as well as the types of materials which can be present within individual wasteforms and maximum limits on the decay heat. (Decay heat is defined as the heat produced by radioactive emissions that is absorbed by the surrounding materials.)

During transportation of cemented wasteforms, the primary mechanism for flammable and non-flammable gas generation is radiolytic decay of hydrogenous (hydrogen-bearing) materials, including plastics, paper, fabrics, rubber, and water. Under conditions of radiolysis such materials undergo decay to simpler products, namely CO, CO_2, free carbon and hydrogen gas. The imposed decay heat limit is intended to minimize the level of flammable gas generation by specifying upper limits on the amount of radioactive material in an individual wasteform. The current limits are based, in part, on the overall hydrogen content. If the hydrogenous content (which would be primarily water) of a Type I cemented wasteform can be reduced to less than 30 percent by weight, then the maximum allowable decay heat for this modified wasteform increases fourfold. Clearly, if the hydrogenous content can be reduced, a greater loading of radioactive material can be achieved, thereby reducing the volume of disposable waste while still meeting transportation requirements.

The hydrogenous content of OPC, largely water, is dictated by processing constraints. A minimum water/cement ratio is necessary to achieve a cement paste sufficiently fluid to permit thorough mixing. There have been extensive studies made on the use of additives to reduce the water content. Various organic plasticizers and inorganic set-retarders have been examined. The addition of organic compounds, however, exacerbates the gas generation problem, while inorganic set retarders, primarily sulfates, result in swelling of the wasteform and occasional rupturing of the drums. Non-portland cements, such as those based on gypsum, have also been evaluated. These wasteforms, however, are prone to incomplete setting in the presence of organics. The final consequence of these investigations is that unmodified OPC remains the matrix of choice for low-level waste immobilization.

III. SUPERCRITICAL FLUIDS

Supercritical CO_2 occurs naturally in the headspace above oil reservoirs, and high-pressure CO_2 has been used for many years by oil producers in secondary and tertiary recovery processes. In addition, supercritical fluids are used as solvents in many commercial applications, including the extraction of caffeine from coffee, fats from foods, and essential oils from plants for use in perfumes. The attractiveness of supercritical fluids as solvents stems from their unique combination of liquid-like and gas-like properties. In this regard, supercritical fluids can be thought of as occupying an intermediate position between gases and liquids. The following, phenomenological description will help to illustrate the concept of a supercritical fluid.

The temperature at which the vapor pressure above a pure liquid reaches one atmosphere is known as the normal boiling point. For water, the normal boiling point at one atmosphere is 100°C. In an *open* container, the temperature of liquid water cannot be raised above 100°C since this would cause the vapor pressure of water to rise above one atmosphere, which would exceed the ambient pressure. If we place a quantity of liquid water in a *sealed* container, however, we can heat to higher temperatures, since there is no longer any limit on the vapor pressure we can attain (assuming that the container does not burst). As we uniformly heat the sealed container, the density of the liquid water decreases through thermal expansion. Simultaneously, the density of the water vapor increases as more molecules leave the liquid and enter the vapor phase. We can continue this heating process until the density of the liquid has been so reduced, and the density of the vapor phase has been so increased, that the two densities become equal. The temperature at which the liquid and vapor densities become equal is called the critical temperature. Since the temperature and density inside our sealed container is equal throughout, the laws of thermodynamics dictate that the pressure inside the container be equal throughout. This pressure is called the critical pressure. A liquid (or gas) which has been brought to conditions above its critical temperature and pressure is known as a supercritical fluid.

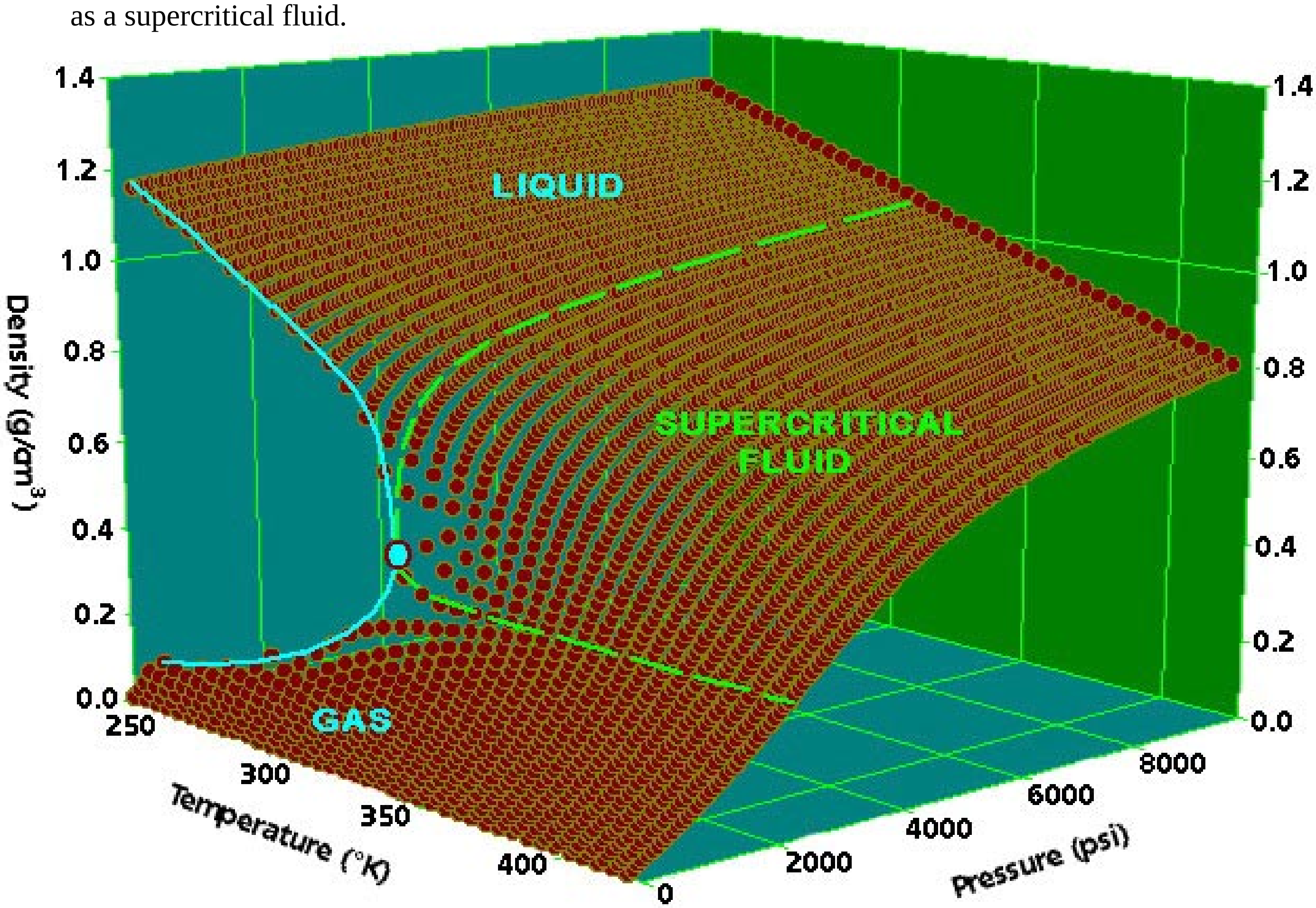

Figure 1. Pressure-Temperature-density surface for pure CO_2.

Figure 1 (previous page) shows the pressure-temperature-density surface for pure CO_2.[4] The critical condition of temperature and pressure (31°C and 1072 psi) is shown in the figure by the solid circle. It can be seen that relatively small changes in temperature or pressure, above the critical values, can result in large changes in density. It is this tunability of density which is one of the most attractive attributes of supercritical fluids. The reason is that, to a first approximation, the ability of a fluid to solubilize other fluids is related to density: higher density results in higher solubilities. Also, the gas-like properties of low viscosity and high diffusivity provides for efficient mass transport into and out of granular and micro-porous matrices, such as cast cements. Finally, the absence of surface tension provides for excellent substrate wetting.

Supercritical CO_2, as a candidate for scale-up to a production treatment process, has several safety and economic advantages. CO_2 is non-toxic, non-flammable, and inexpensive (1040 cents per pound). Its critical conditions of temperature and pressure are easily achievable using readily available process equipment. Also, there is already a transportation infrastructure (virtually all restaurants serve carbonated drinks, which require the use of compressed CO_2 cylinders). It is the goal of our work to use this unique combination of physico-chemical and economic properties of supercritical fluid $SCCO_2$ to enhance the performance of cemented wasteforms.

IV. SUPERCRITICAL FLUID CO_2 TREATMENT OF STANDARD PORTLAND CEMENTS

The natural curing reactions which occur in OPC involve the formation of calcium hydroxide (portlandite), as well as calcium silicate hydrates (CSH). Over time, the cement will abstract CO_2 from the air, converting the calcium hydroxide and CSH to anhydrous calcium carbonate. It turns out, however, that this secondary conversion results in the closure and/or blockage of pores, impeding the ingress of reactants (CO_2) and the egress of reaction products (H2O), drastically slowing the reaction rate with time. It is known that even the oldest cements, thousands of years in age, are still undergoing this natural carbonation reaction. By exposing an OPC to $SCCO_2$ it is found that the carbonation reaction can be greatly accelerated. This acceleration is due to the ease of penetration of the supercritical fluid into the micro-pores of the cement, providing continuous availability of fresh, hyper-stoichiometric reactant, as well as the solubility of the reaction product in the supercritical fluid, facilitating its removal.

Figure 2 (following page) shows a schematic pressure-temperature phase diagram for CO_2, onto which is superimposed a process flow diagram for a closed-loop cement-treatment system. The extraction cycle begins with a liquid-CO_2 storage reservoir. The liquid is brought to above its critical pressure during a pumping operation, which sends the pressurized liquid to a heating unit. The heating unit brings the temperature of the pressurized CO_2 above its critical temperature. The supercritical fluid enters the extraction vessel and is brought into contact with the cement wasteform to be treated. There is a constant flow of CO_2 through the treatment vessel so that clean, dry CO_2 is continuously made available to the cement. In the supercritical state, $SCCO_2$ is a non-polar "organic" solvent. Although water is a polar substance, the high $SCCO_2$ density allows for water solubilities of 0.2-0.5 mole percent, so that a flowing system can remove large amounts of water in relatively short times. On exiting the extraction vessel, the supercritical fluid CO_2 is sent to a separation vessel, where the fluid is de-pressurized to below its critical pressure, reducing the CO_2 density to a gas-like value. The solubility of the entrained materials (water and organics) is greatly

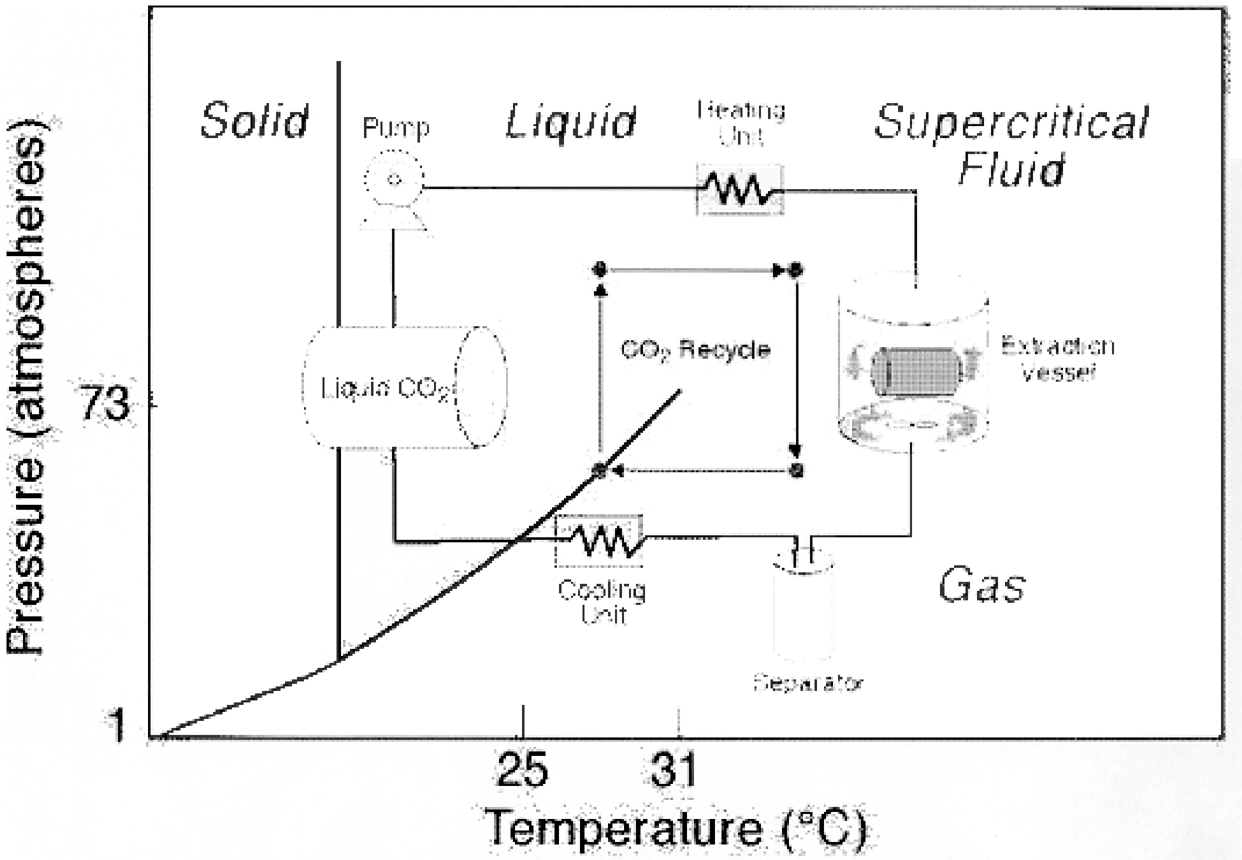

Figure 2. Pressure-temperature diagram for CO_2 with a superimposed closed-loop treatment cycle.

reduced in the low-density gas phase and are deposited in the bottom of the separator. The clean CO_2 gas exits the top of the separator, where it is chilled to liquefaction by a cooling unit before re-entering the storage vessel.

This type of closed-loop treatment, applied to cemented wasteforms, means that there are no waste streams exiting the treatment system. All of the extracted materials are retained in the separation vessel for subsequent analysis, treatment and/or disposal. Further, the extracted materials are concentrated in the separator, reducing the volume of waste. It is important to note that $SCCO_2$, while solubilizing organic compounds and water, is not expected to leach inorganic compounds, as these will be bound up in the crystal structure of the inorganic phases. The projected advantage of this type of $SCCO_2$ treatment scheme, in terms of operations at a radwaste production-facility, is that the cemented wasteforms can continue to be cast using established methods, with the treatment process involving only an additional, post-casting step.

By treating straight OPC, using a closed-loop treatment system like the one shown in Figure 2, we can extract the majority of the hydrogenous material. Our work with 1" x 3" cylinders of OPC shows that nearly complete carbonation (with simultaneous dehydration) can be achieved by a $SCCO_2$ treatment at 4000 psi and 40°C for 2-hours. Measured permeability values for the treated material are reduced by an order of magnitude over untreated values. The porosity values are similarly improved for the treated material. Specific results will be reported in the verbal presentation.

We are currently performing treatment tests on 6" x 12" OPC cylinders. We are measuring the total water and CO_2 content, using a measurement system similar to ASTM standard method D 3178. These studies will quantitatively determine the degree of chemical conversion of the OPC, as a function of the treatment parameters listed below.

Table 2. Relevant issues for the evaluation of supercritical fluid CO_2 to S/S using OPC and fly ash-modified OPC.

supercritical fluid treatment parameters	affected cement properties
• treatment pressure • treatment temperature • treatment time • cement composition	• hydrogenous content • porosity • permeability • mechanical strength • leachability

V. ANTICIPATED USE OF FLY ASH-MODIFIED CEMENTS

The incorporation of fly ash into OPC has been identified as one of the treatment parameters of cement composition to be evaluated. There is already an extensive "experience database" on the performance of fly ash-modified OPC for radwaste immobilization. The United Kingdoms and the United States[6] have used these materials, in the form of cement grouts, for the S/S of low and intermediate-level radioactive wastes. In this section, we will review the known benefits of fly ash-modified OPC over straight OPC, along with the anticipated improvements expected by the treatment of modified OPC with $SCCO_2$.

- Fly ash increases the density, decreases the permeability, and increases the leaching resistance of OPC. It is a truism that "The leach resistance of solidified cement-waste systems can be improved by any process which accelerates curing, limits porosity, or chemically bonds fission product or actinide elements."[7] $SCCO_2$ treatment of a modified OPC is expected to further increase the density over the untreated material, so that a reduced porosity, and improved leachability should result. In addition, the high silica content of fly ash, with its well-known sorbent properties towards plutonium and certain other radionuclides, should also enhance the immobilization characteristics.

- The incorporation of fly ash into OPC helps to partially compensate for the set-retarding effect of heavy and non-noble metals. Although the reduction hydrogenous material content resulting from $SCCO_2$ treatment of an OPC will allow for increased actinide loadings, the higher metals content may significantly interfere with proper setting. Fly ash-modified cements perform somewhat better in this regard, and a $SCCO_2$ treatment of a modified cement should be even better.

- Fly ash incorporation increases OPC mix fluidity, which improves workability. For S/S applications, the increased fluidity may allow a reduced water/cement ratio to be used in the casting operation. Since the casting is done in a glovebox environment, the need to maintain process simplicity is paramount.

- The incorporation of fly ash lowers the initial heat evolution during setting, reducing the incidence of cracking and spelling. It is desirable to maintain the wasteform in monolithic form for optimum leach resistance.

- Fly ash, as it is typically generated in a high free-carbon environment, contains iron in a reduced state, which helps to lower the redox potential in the cement. As is the case for regulated heavy metals, such as Cr, maintaining the actinides in lower oxidation states should result in lower solubilities. We hasten to point out that one of the major unanswered questions regarding the use of $SCCO_2$ for the treatment of cemented wasteforms is the effect of the altered pH on actinide solubility. In OPC, the highly alkaline environment precipitates the actinides as hydroxides, rendering them immobile. Since the $SCCO_2$ treatment converts the alkaline phases into neutral pH phases, a straight or fly ash-modified OPC which has been treated will have a much reduced pH. An thorough investigation of this solubility issue is essential.

- While portland cement is considered to be an inexpensive immobilization matrix, relative to other candidate materials, its cost is expected to rise in light of current and future projected shortages. Fly ash, as it is a large-volume industrial waste, is both cheap and abundant, so that there is an economic incentive to use fly ash-modified cements. In addition, CO_2 is also produced as a waste by-product of industrial processes (power generation, cement manufacture, *etc*,), and its permanent sequestration into cement is an added environmental benefit.

VI. CONCLUSIONS

Although cementation is a standard S/S treatment process, many cemented wasteforms are failing to qualify for underground disposition because of transport and/or disposal requirements. We have been evaluating supercritical CO_2 carbonation of OPC to alter the bulk phase chemistry, which accelerates the natural aging (carbonation) reactions. This treatment process produces a chemically stable form having substantially-reduced levels of free liquids and organics, as well as reduced porosity, permeability and pH. The promising results obtained with $SCCO_2$ treatment of OPC leads us to speculate that fly ash-modified OPC may produce a highly efficient immobilization matrix. The structural and chemical changes produced by the treatment process should allow for a reduction on waste volume and a reduced mobility of anions, cations, and radionuclides in aboveground and underground repositories.

VII. REFERENCES

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